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03 Coordination Compounds

Introduction and terminology and classification of ligands

Introduction

(a) The concept of coordination compounds arises from the complex formation tendency of transition elements.

(b) These compounds play a vital role in our lives. Haemoglobin of blood and chlorophyll of plants are also coordination compounds of Fe, Mg respectively.

Type of compounds

Molecular or Addition Compounds

(a) When two or more simple salts are chemically combined together in fixed proportion by weight the molecular or addition compounds are formed.

(b) Some common examples are as follows.

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow \underset{\text{Alum}}{K_2SO_4.Al_2(SO_4)_3.\ 24H_2O}$$

(c) Depending upon the behaviour in an aqueous solution they are of two types

(i) Double salt

(ii) Coordination or complex compounds.

(I) Double Salt

The addition compounds which loose their identity in aq. solution and get completely ionised in water.

Ex. (i) $K_2SO_4.Al_2(SO_4)_3.24H_2O$ (Potash Alum)

(ii) $FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr's salt)

(iii) $KCl.MgCl_2.6H_2O$ (Carnallite)

(II) Coordination or Complex Compounds

(i) Those molecular or addition compounds which retain their identity in aq. solution or loose the identity of constituents are called complex salt.

(ii) Complexes retain their identity in aqueous solution. i.e., they do not dissociate into separate ion.

$$\underset{\text{Potassium ferrocyanide}}{K_4[Fe(CN)_6]} \xrightarrow{H_2O} 4K^+ + \underset{\text{Ferrocyanide ion}}{[Fe(CN)_6]^{-4}}$$

(iii) On the basis of type of ligands complex compounds are divided as follows :

(i) Homoleptic complexes :

Complex in which all the ligands are identical is called homoleptic complex.

Ex. $[Co(NH_3)_6]^{+2}$

(ii) Heteroleptic complexes :

Complex in which all the ligands are not identical is known as heteroleptic complex.

Ex. $[Fe(en)_2Cl_2]^{+1}$

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Terminology of complex compounds

(A) Complex Ion/Coordination sphere

(a) An aggregate of metal ion with anions, cation or neutral molecules is called as **complex ion.**

(b) It is a non-ionisable part of complex compound.

(B) Central Metal Ion

(a) The metal ion which forms complex ion in combination with anions, cation or neutral molecules is called as **central metal ion**.

(b) Central metal ion acts as an electron pair acceptor and forms coordinate bonds with donor species.

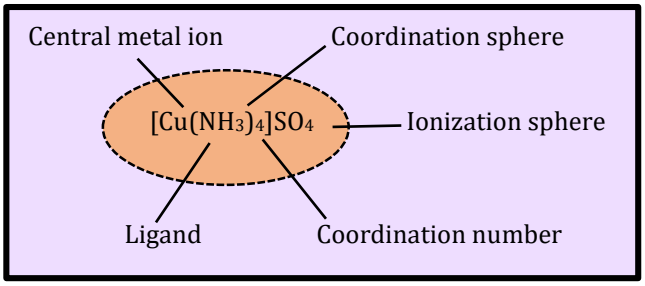
(c) Generally belongs to d block because d block elements have tendency to form complex due to their high charge density and availability of vacant orbitals.

(C) Coordination Number

The total number of coordinate bonds formed by central metal ion with donor species is called as coordination number of central metal ion.

(D) Ionisation Sphere

The part of complex compound which get ionised is known as ionisation sphere.



(E) Oxidation State

It is a number which represents the electrical charge on the central metal atom of a complex ion.

Ex. the oxidation number of Fe, Co and Ni in $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$ and $Ni(CO)_4$ is +2, +3 and zero respectively.

(F) Charge On the Complex Ion

It is the algebraic sum of the total charge of the donor species and central metal ion.

(G) Ligands

(a) The anions, cation or neutral molecules which combine with central metal ion to form complex ion are called as ligands.

(b) They act as electron pair donor (Lewis bases) which donate e^- pair to central metal ion and form coordinate bonds.

(c) Number of e^- pair donated by a ligand to central metal ion is equal to its denticity.

(H) Naming of ligands

(a) o-suffix is used in the name of anionic ligands.

(b) ium-suffix is used in the name of cationic ligands.

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Classification of ligands :- On the basis of denticity.

1. **Monodentate ligands :** Which donate one e^- pair to the central metal ion.

Neutral monodentate ligands	
NH_3	ammine
H_2O	aqua
NO	nitrosyl
PH_3	phosphine
PPh_3	triphenyl phosphine
O_2	dioxygen
N_2	dinitrogen
$CH_3–OH$	methyl alcohol
$CH_3–NH_2$	methyl amine
NH_2CONH_2	urea
NH_2NH_2	hydrazine
$CH_3–O–CH_3$	dimethyl ether
CO	carbonyl
CS	thiocarbonyl

Cationic monodentate ligands :	
O_2^+	oxygenium
NO^+	nitrosylium or nitrosonium
NO_2^+	nitronium
$N_2H_5^+$	hydrazinium

Anionic monodentate ligands :	
F^-	Fluorido / fluoro
Cl^-	Chlorido / chloro
Br^-	bromido / bromo
I^-	iodido / iodo
O^{-2}	oxido/oxo
S^{-2}	sulphido/sulpho
OH^-	hydroxido / hydroxo
O_2^-	superoxido / superoxo
O_2^{-2}	peroxido / peroxo
N^{-3}	nitrido
N_3^-	azido
$(NH_2)^-$	amido
NH^{-2}	imido
H^-	hydrido

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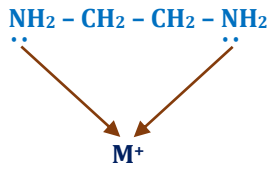
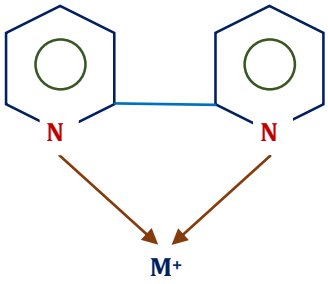
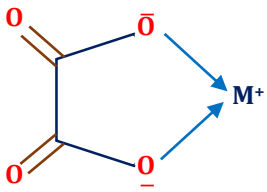
2. **Bidentate ligands :** Ligands which donates two e^- pair to the central metal ion.
Ligands having denticity 2 or more than 2 form a stable ring with central metal ion that's why they are known as chelating ligands.
no. of rings = Denticity – 1



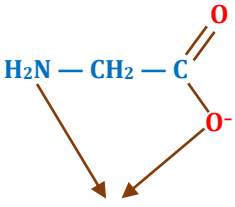
Ethylene diamine (en)



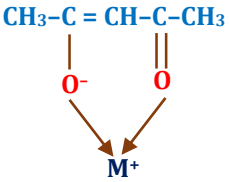
dipyridyl (dipy)



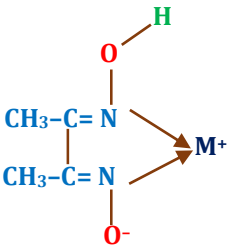
oxalate(ox) or $C_2O_4^{-2}$



glycinato(gly)⁻
(unsymmetrical)

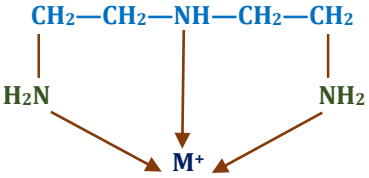


acetyl acetonato (acac)⁻

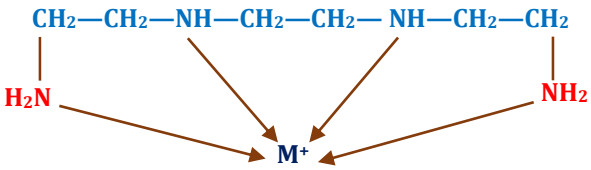


dimethyl glyoximato (dmg)⁻

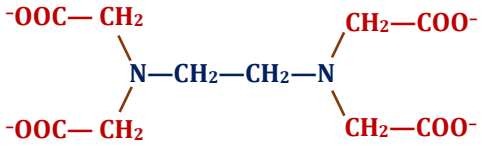
3. **Polydentate ligands**



Diethylenetriamine(dien)
Tridentate



Triethylenetetraamine (trien)
Tetradentate



Ethylene diaminetetraacetato ($EDTA^{4-}$)
Hexadenatate

4. **Ambidentate ligand:** Ligands which have two different donor atoms but at one time one donor atom can donate electron pair are called ambidentate ligands.
Ambidentate ligands have same molecular formula but have different donor atom.

(i)	$M \leftarrow \bar{C} \equiv N$	cyanido (CN)
	$M \leftarrow N \equiv \bar{C}$	isocyanido(NC)
(ii)	$M \leftarrow \bar{O} - C \equiv N$	cyanato / cyanato-O
	$M \leftarrow N \equiv C - \bar{O}$	isocyanato / cyanato-N
(iii)	$M \leftarrow \bar{S} - C \equiv N$	Thiocyanato / Thiocyanato-S
	$M \leftarrow N \equiv C - \bar{S}$	Isothiocyanato/thiocyanato-N

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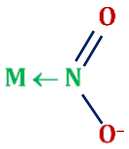
(iv) $M \leftarrow \overline{O} - N = O$ Nitrito / Nitrito-O



Nitro / Nitrito-N

5. **Flexidentate ligands :** Ligands which can change their denticity.

SO_4^{-2}, $S_2O_3^{-2}$, CO_3^{-2}, NO_3^-, CH_3COO^- etc are generally act as monodentate ligand but in some compound they can act as bidentate ligand.

e.g. **(i)** $[Co(NH_3)_5(SO_4)]Cl$ in this complex SO_4^{-2} act as a monodentate ligand.

(ii) $[Co(en)_2(SO_4)]Cl$ in this complex SO_4^{-2} act as a bidentate ligand.

Classification of ligands – synergic bonding

On the basis of nature of bonding between central metal atom and ligand:-

(i) **Normal or classical ligands**:

Ligand which only donate electron pair to central metal ion & form coordinate (σ) bond

e.g. OH^-, NH_2^-, Cl^-, N^{-3}, O^{-2} etc.

(ii) **Non classical or π-acid or π-acceptor ligands :-**

Ligand which donate electron pair to central metal ion & form coordinate σ bond but simultaneously they accept electron pair from central metal ion through back bonding or synergic bonding.

e.g. CO, NO^+, CN^-, R_3P, R_3As etc.

Synergic bonding in metal carbonyls

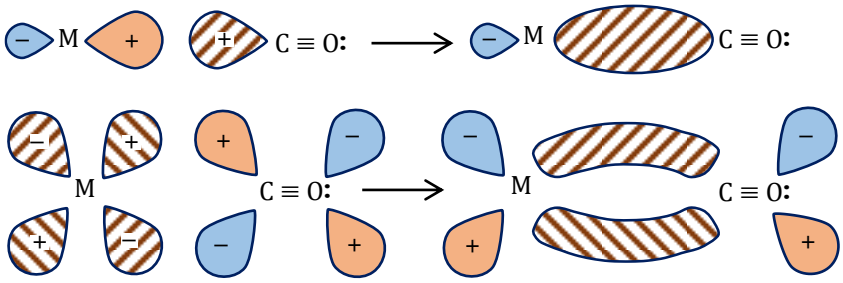
They are of 2 types:-

(a) **σ donor and π acceptor ligands**

Ligands which donate their lone pair to central metal ion through σ bond and simultaneously accept e^- pair from central metal ion through π bond.

The electronic configuration of CO molecule shows that it has lone pair of electrons on carbon and oxygen atom each. Carbon atom can donate its electron pair of a transition metal atom (M), forming OC→M coordinate bond.

Since the metal atom in metal carbonyl is in zero oxidation state, the formation of M ← CO σ bond accumulates a negative charge on the metal atom. The accumulation of negative charge on the metal atom can be counter balanced by transferring some negative charge from the metal atom to CO molecule (ligand). This transfer can be done by making a M → CO π bond by the overlap between an appropriate filled d orbital on the metal atom and empty π_y^* or π_z^* molecular orbital of CO molecule. This type of bonding between M and CO is called **synergic bonding.**



[Schematic of orbital overlaps in metal carbonyls]

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Conclusion of synergic bonding :

(I) M–C bond strength increases; M–C bond length decreases; because double bond character increases

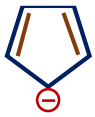
(II) C–O bond strength decreases; C–O bond length increases; because bond order of C–O decreases (CO accepts e^- pair into its antibonding molecular orbital)

(III) **π-donor and π-acceptor ligands**

Ligands which donate π electron pair to central metal ion & also accept electron pair from central metal ion through synergic bonding.

(i) $H_2C=CH_2$ (η^2 - ethylene) : it is a 2π electron donor

(ii) (η^6 - benzene) : it is a 6π electron donor

(iii)  / $[C_5H_5]^-$ (η^5 -cyclopentadienyl) : it is a 6π electron donor

for example

(i) $[Cr(\eta^6-C_6H_6)_2]$

sandwich compound

(Chromocene)

(ii) $[Fe(\eta^5-C_5H_5)_2]$ ferrocene (sandwich compound)

(iii) $K[PtCl_3(\eta^2-C_2H_4)]$ (Zeise's salt)

BEGINNER'S BOX-1

1. Which of the following is true about metal-EDTA complex (if it is a 3d metal)

(1) The ratio of moles of metal & EDTA in complex is 1:6

(2) The ratio of moles of metal & EDTA in complex is 6:1

(3) The ratio of moles of metal & EDTA in complex is 1:1

(4) 3d metal ion cannot bonded with EDTA

2. CN^- is an ambidentate ligand because

(1) It has multiple bonds

(2) Carbon has a negative charge

(3) It form chelate

(4) Both C & N can donate lone pair

3. The strongest CO bond is present in

(1) $[Cr(CO)_6]^+$

(2) $[Fe(CO)_5]$

(3) $[V(CO)_6]^-$

(4) All have equal strength

4. Match the following and choose correct option.

Ligand	**Property**
(A) Ethylenediamine	(P) Bidentate ligand
(B) Hydrazene	(Q) Tridentate ligand
(C) Dimethylgyloximato(dmg^-)	(R) Monodentate ligand
(D) Dien	(S) Can form hydrogen bond

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	A	B	C	D
(1)	P	Q	R	S
(2)	P	R	Q	S
(3)	P	R	S	Q
(4)	P	S	Q	R

5. Which ligand is non classical ligand

(1) Cl^- (2) CO (3) OH^- (4) NH_3

6. $H_2N - CH_2 - CH_2 - NH_2$ serves as :

(1) Monodentate ligand (2) Chelating ligand (3) Anionic ligand (4) Cationic ligand

7. An incorrect statement is :

(1) The metal-carbon bond in metal carbonyls posess both σ and π character.

(2) The M-C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π* orbital of carbon monoxide.

(3) The metal to ligand bonding creates a synergic effect which strengthens the bond between C – O in CO.

(4) Due to M-C π bond the C – O bond order decreases and M – C bond length decreases.

Calculation of Oxidation Number, Coordination Number And No. of Chelate Ring

Number of chelate ring (C.R.) = denticity – 1

Coordination no. (C.N.) = total no. coordinate bonds formed by ligands with CMA

Oxidation no. (O.N.) = total charge on CMA

Example

(1) **$K_4[Fe(CN)_6]$**

$+ 4 + x - 6 = 0$

$x = +2$

(a) O.N. of Fe is +2

(b) CN^- is a monodentate ligand.
C.N. of Fe = $1 \times 6 = 6$

(c) No. of chelate ring = 1–1 = 0

(2) **$[Cu(NH_3)_4]SO_4$**

$x + 0 - 2 = 0$

$x = +2$

(a) O.N. of Cu is +2

(b) NH_3 is a monodentate ligand
C.N. of Cu = $1 \times 4 = 4$

(c) No. of chelate ring = 1–1 = 0

(3) **$[Co(en)_3]Cl_3$**

$x + 0 - 3 = 0$

$x = +3$

(a) O.N. of Co is +3

(b) en is a bidentate ligand
C.N. of Co = $2 \times 3 = 6$

(c) No. of chelate ring = 2–1 = 1×3 =3

(4) **$[Cu(dien)_2]SO_4$**

$x + 0 - 2 = 0$

$x = +2$

(a) O.N. of Cu is +2

(b) dien is a tridentate ligand
C.N. of Cu = $3 \times 2 = 6$

(c) No. of chelate ring = $3 - 1 = 2 \times 2 = 4$

(5) **$[Ca(EDTA)]^{2-}$**

$x - 4 = -2$

$x = +2$

(a) O.N. of Ca is +2

(b) $EDTA^{4-}$ is a hexadentate ligand.
C.N. of Ca = $1 \times 6 = 6$

(c) No. of chelate ring = 6 – 1 = 5

(6) **$K_3[Co(ox)_3]$**

$+3 + x - 6 = 0$

$x = +3$

(a) O.N. of Co is +3

(b) ox is a bidentate ligand
C.N. of Co = $2 \times 3 = 6$

(c) No. of chelate ring = $2 - 1 = 1 \times 3 = 3$

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IUPAC Nomenclature

IUPAC Nomenclature of coordination compounds

The present system of nomenclature derived from the suggestions of **Alfred Werner** and recommended by the Inorganic Nomenclature Committee of the I.U.P.A.C. The main rules of naming of complexes are -

(a) Like simple salts, the positive part of the coordination compound is named first.
Ex. $K_4[Fe(CN)_6]$ the naming of this complex starts with Potassium.

(b) In the naming of complex ion, ligands are to be named before the naming of central metal ion.

(c) If no. of ligands are more than one then their presence is indicated by prefixes like di, tri, tetra etc. but in case of polydentate ligands different prefixes such as bis, tris are used.

(d) When more than one type of ligand is present in the complex, then the ligands are named in the alphabetical order.

(e) If the complex is neutral or cationic then the central metal ion is to be named as it is.
If the complex is anionic complex then the name of central metal ion ends in 'ate'

(f) After the naming of central metal ion, oxidation state of central metal ion is written in Roman numeral.
The naming of some of the complexes is done as follows – (as per IUPAC)

Complex Compounds	IUPAC Name
(i) $K_4[Fe(CN)_6]$	Potassium hexacyanidoferrate (II)
(ii) $K_2[HgI_4]$	Potassium tetraiodidomercurate (II)
(iii) $[Co(NH_3)_6]Cl_3$	Hexamminecobalt (III) chloride
(iv) $[Cr(H_2O)_4Cl_2]Cl$	Tetraaquadichlorochromium (III) chloride
(v) $[Pt(NH_3)_2Cl_4]$	Diammine tetrachloroplatinum (IV)
(vi) $[Co(NH_3)_3Cl_3]$	Triamminetrichlorocobalt (III)
(vii) $K_3[Co(NO_2)_6]$	Potassium hexanitrocobaltate (III)
(viii) $Na_2[Fe(CN)_5NO]$	Sodium pentacyanonitrosoniumferrate (II)
(ix) $[NiCl_4]^{-2}$	Tetrachloronickelate(II) ion
(x) $[Ru(NH_3)_5Cl]^{+2}$	Pentamminechlororuthenium (III) ion
(xi) $[Fe(en)_3]Cl_3$	Tris (ethylenediamine) iron (III) chloride

(g) If coordination compound contains 2 coordination spheres then both spheres should have opposite charges. Name of cationic part is written first following the name of anionic sphere according to the general IUPAC rule.
e.g. $[Pt(NH_3)_4]^{+2}\ [PtCl_4]^{-2}$
Tetraammineplatinum (II) tetrachloroplatinate (II)

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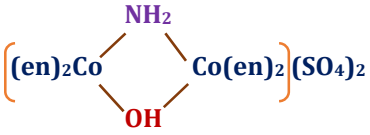
(h) If in a complex compound bridging ligands is present then μ – prefix is used before its name.
bis (ethylene diamine) cobalt (III) – μ–amido–μ–hydroxo bis (ethylenediamine) cobalt (III) sulphate



Effective atomic number

Effective atomic number (EAN)→ Total no. of e^- associated with central metal ion in a complex is equal to effective atomic number.

EAN = Atomic number – (Oxidation state) + (2 × Coordination number)

Examples :

Complex	Metal (Oxidation State)	Atomic Number of Metal	Coordination number	Effective atomic number (E.A.N)
$[Cu(NH_3)_4]SO_4$	+2	29	4	(29–2) + (4×2) = 35
$[Co(NH_3)_6]Cl_3$	+3	27	6	(27–3) + (6×2) = 36
$K_2[Hg(I)_4]$	+2	80	4	(80–2) + (4×2) = 86
$[Ag(NH_3)_2]Cl$	+1	47	2	(47–1) + (2×2) = 50

Werner's Theory

This was postulated by **Alfred Werner** in 1893. The postulates of Werner's theory of complexes are–
According to Werner central metal atom in a complex compound have 2 types of valencies :

Primary Valency	Secondary Valency
(1) It is the oxidation number of Central metal ion.	(1) It is the coordination number of Central metal ion.
(2) It is satisfied by negative charged species.	(2) It is satisfied by negative, positive and neutral species.
(3) Ionizable	(3) Non-ionizable
(4) Non-directional	(4) Directional
(5) It can't predict the geometry of complex	(5) Define the geometry of complex
(6) Denoted by dash lines	(6) Denoted by solid lines.

Experimental evidence of Werner's theory

(a) Precipitation of primary valencies on the addition of suitable reagent. In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding silver nitrate solution but some remained in solution.

1 mole $CoCl_3 \cdot 6NH_3 \xrightarrow{AgNO_3}$ 3 moles of AgCl white ppt

hence $CoCl_3 \cdot 6NH_3$ is formulated as $[Co(NH_3)_6]Cl_3$

Which ionises as $[Co(NH_3)_6]^{+3}\ 3Cl^-$ (4 mole ions)

1 mole $CoCl_3 \cdot 5NH_3 \xrightarrow{AgNO_3}$ 2 moles of AgCl

hence $CoCl_3 \cdot 5NH_3$ is formulated as $[Co(NH_3)_5Cl] \cdot Cl_2$

Which ionises as $[Co(NH_3)_5Cl]^{+2}\ 2Cl^-$ (3 mole ions)

1 mole $CoCl_3 \cdot 4NH_3 \xrightarrow{AgNO_3}$ 1 moles of AgCl

hence $CoCl_3 \cdot 4NH_3$ is formulated as $[Co(NH_3)_4Cl_2] \cdot Cl$

Which ionises as $[Co(NH_3)_4Cl_2]^+\ Cl^-$ (2 mole ions)

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(b) Electrical conductance of complexes

More the number of ions provided in aqueous solution greater will be electrical conductance of the complex in aqueous solution.

e.g. order of electrical conductance is

$CoCl_3 \cdot 6NH_3 > CoCl_3 \cdot 5NH_3 > CoCl_3 \cdot 4NH_3$

BEGINNER'S BOX-2

1. The oxidation state of Iron in $[Fe(CN)_6]^{3-}$ is
(1) –6 (2) +3 (3) – 3 (4) + 6

2. Coordination number of Co in $[CoF_6]^{3-}$ is
(1) 4 (2) 5 (3) 6 (4) 8

3. The IUPAC name of $Fe(CO)_5$ is
(1) Pentacarbonyl ferrate (0)
(2) Pentacarbonyl Ferrate (III)
(3) Pentacarbonyl Iron (0)
(4) Pentacarbonyl Iron (II)

4. The compound $Na_2[Fe(CN)_5NO]$ is called
(1) Sodium pentacyanonitrosonium ferrate (II)
(2) Sodium nitroprusside
(3) Sodium nitrosoferrocyanide
(4) 1 & 2 both

5. $FeCl_3.4H_2O$ is actually :
(1) $[Fe(H_2O)_4]Cl_3$
(2) $[Fe(H_2O)_3Cl]Cl_2.H_2O$
(3) $[Fe(H_2O)_4Cl_2]Cl$
(4) $[Fe(H_2O)_3Cl_2]Cl.H_2O$

6. Which of the following compound does not give test of chloride ion in aqueous solution
(1) $CoCl_3.6NH_3$ (2) $CoCl_3.5NH_3$ (3) $CoCl_3.4NH_3$ (4) $CoCl_3.3NH_3$

7. Which of the following is most likely formula of platinum complex, if $\frac{1}{4}$ of total chlorine of the compound is precipitated by adding $AgNO_3$ to its aqueous solution
(1) $PtCl_4.6H_2O$ (2) $PtCl_4.5H_2O$ (3) $PtCl_2.2H_2O$ (4) $PtCl_4.3H_2O$

8. The Effective atomic number of Cr in $Cr(CO)_6$ is
(1) 36 (2) 38 (3) 28 (4) 54

9. Which complex is chelating complex ?
(1) Diammine dichloroplatinum (II)
(2) Bis (ethylene diamine) copper (II)
(3) Tetra carbonyl nickel (0)
(4) Hexacyanoferrate (III) ion

10. The Effective atomic number of iron in $K_4[Fe(CN)_6]$ is :
(1) 35 (2) 34 (3) 36 (4) 38

11. Which of the following represent the correct number of ions formed by the given compounds in aqueous solution?
(i) $PdCl_2.4NH_3$ (ii) $NiCl_2.6H_2O$ (iii) $PtCl_4.2HCl$ (iv) $CoCl_3.4NH_3$
(v) $PtCl_2.2NH_3$
(1) 0, 3, 0, 2, 3 (2) 3, 3, 3, 2, 0 (3) 3, 3, 3, 2, 3 (4) 0, 3, 3, 3, 3

12. Which of the following does not follow EAN rule ?
(1) $[Ni(CO)_4]$ (2) $[Fe(CO)_5]$ (3) $[Cr(CO)_6]$ (4) $[Mn(CO)_5]$

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Valence Bond Theory (VBT)

VBT Postulates

This theory was mainly developed by **Linus Pauling**. The main features of this theory are -

(a) Metal ion when it forms a complex compound undergoes formation of coordinate bond.

(b) During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals according to its coordination number.

(c) **Ex.** In the formation of $[Fe(NH_3)_6]^{3+}$, Fe^{+3} ion provides six vacant orbitals.
In $[Cu(NH_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.

(d) These vacant orbitals undergo hybridisation before bond formation with ligands.

(e) The vacant hybrid orbitals of metal ion get overlapped with orbitals of ligands containing lone pair of electrons.

(f) If in a complex strong ligand is present then it will cause pairing of unpaired e^- in (n–1)d orbitals of central metal ion and if (n–1)d orbitals are involved in hybridisation then inner orbital complex is formed.

(g) If in the complex weak ligand is present then there will be no pairing of unapaired e^- in (n–1)d orbitals and if nd orbitals are involved in hybridisation, outer orbital complex is formed.

(h) If unpaired e^- is present in the complex then it will be paramagnetic otherwise it will be diamagnetic.

VBT Applications

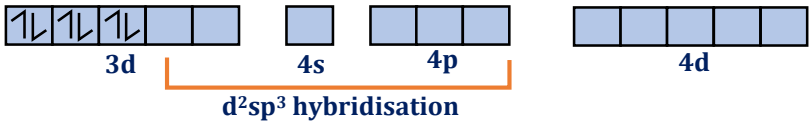
(a) **6-coordinated complexes :**

$[Co(NH_3)_6]^{3+}$

e^- configuration of $_{27}Co = [Ar]\ 3d^7\ 4s^2$ So, $Co^{+3} = [Ar]\ 3d^6\ 4s^0\ 4p^0\ 4d^0$

Co^{3+}

Due to presence of strong ligand unpaired electrons get paired up so metal ion provides vacant '3d' orbitals for hybridisation.



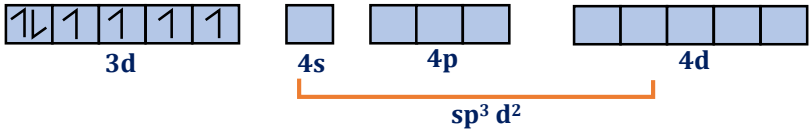
- This is a **diamagnetic complex** and **low spin complex.**
- As inner 'd' orbitals are involved in hybridisation, hence it is an **inner orbital complex**.

$[CoF_6]^{3-}$

e^- configuration of $_{27}Co = [Ar]\ 3d^7 4s^2$ $\therefore$ $Co^{+3} = [Ar]\ 3d^6\ 4s^0\ 4p^0\ 4d^0$

Co^{3+} ion

$\because$ F^- is a weak ligand, so unpaired e^- do not get paired up and vacant 4d orbitals involved in hybridisation.



- This is a **paramagnetic complex** and **high spin complex.**
- The outer 'd' orbitals are involved in hybridisation, hence it is an **outer orbital** complex.

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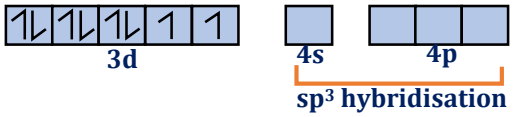
(b) 4-coordinated complexes :

$[NiCl_4]^{2-}$

e^- configuration of $_{28}Ni$ = [Ar] $3d^8\ 4s^2$

$\therefore$ Ni^{+2} = [Ar] $3d^8\ 4s^0\ 4p^0$

- There will be no pairing of unpaired e^- in 3d orbitals.

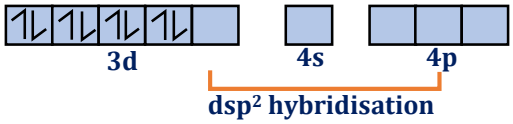


- $[NiCl_4]^{2-}$ has **tetrahedral geometry**.
- It is a paramagnetic complex.

$[Ni(CN)_4]^{2-}$

$_{28}Ni$ = [Ar] $3d^8 4s^2$ Ni^{+2} = [Ar] $3d^8 4s^0 4s^0$

CN^- is a strong ligand so unpaired e^- in 3d orbitals get paired up



- $[Ni(CN)_4]^{2-}$ has square planer geometry and diamagnetic in nature.
- This complex is an **inner orbital complex**

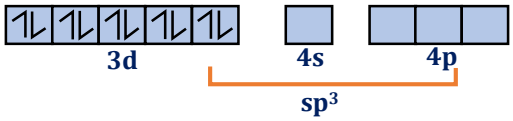
$[Zn(NH_3)_4]^{2+}$

Zn = [Ar] $4s^2\ 3d^{10}$

$\therefore$ Zn^{+2} = [Ar] $3d^{10} 4s^0 4p^0$

$\because$ Zn^{+2} has d^{10} configuration

So there is no possibility of pairing



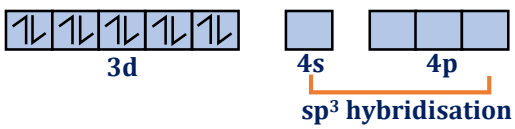
- Because the complex is formed by sp^3 hybridisation, hence it has **tetrahedral geometry**.
- Since all electrons are paired, hence it is **diamagnetic**

$[Ni(CO)_4]$

Ni = [Ar] $3d^8\ 4s^2\ 4p°$

$\because$ CO is a strong ligand so unpaired e^- in (n–1)d orbitals get paired up (4s electron transfer in 3d subshell).

Ni =



- Complex has sp^3 hybridisation
- It has tetrahedral geometry.

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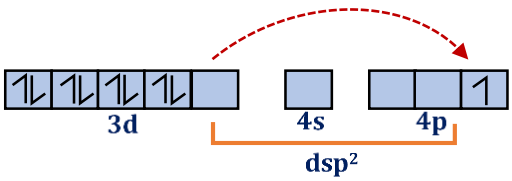
- It is diamagnetic complex as unpaired e^- is absent.

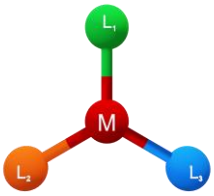
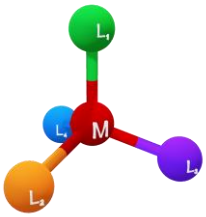
  $[Cu(NH_3)_4]^{2+}$

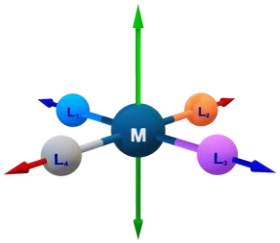
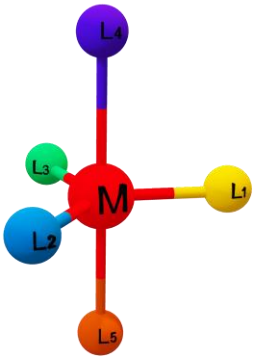
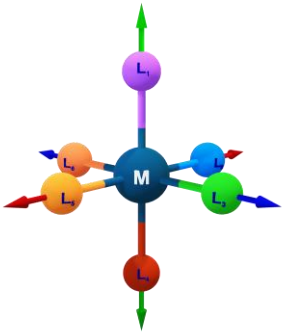
  $_{29}Cu = [Ar]\ 4s^1\ 3d^{10} \therefore Cu^{+2} = [Ar]\ 3d^9\ 4s^0\ 4p^0$

$\because$ NH_3 is a strong ligand so after rearrangement

- Complex has dsp^2 hybridsation
- It is inner orbital complex
- It has square planer geometry
- It is paramagenetic



Coordination Number	Hybridised orbital	Geometrical shape of the Complex	Examples of Complex
2	sp	linear	$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
3	sp^2	 Trigonal planar	$[HgI_3]^-$
4	sp^3	 Tetrahedral	$[CuCl_4]^{-2}$ $[ZnCl_4]^{-2}$ $[Ni(CO)_4]$ $[Zn(NH_3)_4]^{+2}$

4	dsp^2 $\left(d_{x^2-y^2}\text{ orbital}\right)$	 Square planar	$[PdCl_4]^{2-}$
			$[Ni(CN)_4]^{2-}$
			$[Pt(NH_3)_4]^{+2}$
			$[Cu(NH_3)_4]^{+2}$
			$[PtCl_4]^{2-}$
5	dsp^3/ sp^3d	 T.B.P.	$[Fe(CO)_5]$
6	d^2sp^3/sp^3d^2	 Octahedral	$[Cr(NH_3)_6]^{+3}$

Inner orbital Complexes :- When Inner d-orbital or (n–1)d orbital used in a Hybridisation.
It means Hybridisation is d^2sp^3.
$[Cr(NH_3)_6]Cl_3$, $K_4[Fe(CN)_6]$ etc.

Outer-orbital complex :- When outer d-orbital or 'n' d orbital used in a hybridisation. It means Hybridisation is sp^3d^2, $[CoF_6]^{3-}$, $[FeF_6]^{3-}$.

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BEGINNER'S BOX-3

1. Complex ion having square planar geometry is :-
(1) $[Ni(CN)_4]^{2-}$ (2) $[Pt(CN)_4]^{-2}$ (3) $[Cu(NH_3)_4]^{+2}$ (4) All

2. For the complex $[Fe(CO)_5]$ what is wrong :-
(1) It is σ-π bonded organometallic compound (2) It does not follow EAN rule
(3) In the complex CO is π-acid ligand (4) It has trigonal bipyramidal shape

3. In the complex ion $[FeF_6]^{-3}$, according to valence bond theory, the magnetic properties of the complex ion corresponds to how many unpaired electrons ?
(1) 0 (2) 5 (3) 2 (4) 3

4. Among $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$ and $[Ni(Cl)_4]^{2-}$:
(1) $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic
(2) $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[Ni(CO)_4]$ is paramagnetic
(3) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^{2-}$ is paramagnetic
(4) $[Ni(CO_4)]$ is diamagnetic and $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic

5. Which is correct geometry of $[NiCl_4]^{2-}$ complex ?
(1) Tetrahedral (2) Octahedral (3) Square planar (4) Pyramidal

6. Which of the following compound is square planar and does not have any unpaired electron:
(1) $[Cu(NH_3)_4]^{+2}$ (2) $[Ni(CO)_4]$ (3) $[NiCl_4]^{-2}$ (4) $[Ni(CN)_4]^{-2}$

7. Match list - I with list - II and choose the correct answer from the code given below

List - I (complex)	**List - II (geometry)**
(A) $[Ni(CN)_4]^{-2}$	(a) Octachedral
(B) $[Pt(NH_3)_6]^{+4}$	(b) Squareplanar
(C) $[Ag(NH_3)_2]^{+}$	(c) Tetrahedral
(D) $[Zn(NH_3)_4]^{+2}$	(d) Linear

	A	**B**	**C**	**D**
(1)	b	a	d	c
(2)	a	b	c	d
(3)	c	d	b	a
(4)	b	c	d	a

8. Choose the set containing incorrect statement only.
(I) $[Fe(CN)_6]^{-3}$ has magnetic moment is equal to 1.73 BM while $[FeF_6]^{-3}$ has a magnetic moment is equal to 5.9 BM.
(II) $[CoF_6]^{-3}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{-3}$ has two unpaired electrons
(III) $[Co(H_2O)_6]^{+3}$ & $[Co(C_2O_4)_3]^{-3}$ are inner orbital complexes.
(IV) $[Mn(H_2O)_6]^{+3}$, $[Cr(H_2O)_6]^{+3}$ & $[V(H_2O)_6]^{+3}$ are outer orbital complexes with four, three and two unpaired electrons respectively
(1) I, II & III (2) II & IV (3) I & III (4) II, III & IV

9. Which pair of complexes has inner orbital complexes ?
(1) $[Fe(CN)_6]^{-3}$ & $[FeF_6]^{-3}$ (2) $[CoF_6]^{-3}$ & $[CoCl_6]^{-3}$
(3) $[Zn(NH_3)_6]^{+2}$ & $[Zn(H_2O)_6]^{+2}$ (4) $[Fe(CN)_6]^{-3}$ & $[Fe(CN)_6]^{-4}$

10. Which is not related with complex $[Ni(CO)_4]$:-
(1) It has sp^3 hybridisation (2) It has tetrahedral geometry
(3) It is paramagnetic (4) It is diamagnetic

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Crystal field theory (CFT)

Crystal Field Theory : This is a model of electronic structure of transition-metal complexes that considers how the energies of the d-orbitals of a metal ion are affected by the electric field of the ligand. According to this theory.

(a) Central metal ion is considered as a positive point charge, anionic ligand as a negative point charge, neutral ligand as a point dipole and attraction between metal ion and ligand is electrostatic in nature.

(b) In the electric field of ligands, the five d orbitals of the metal atom no longer have exactly same energy while they are splitted into different energy levels. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

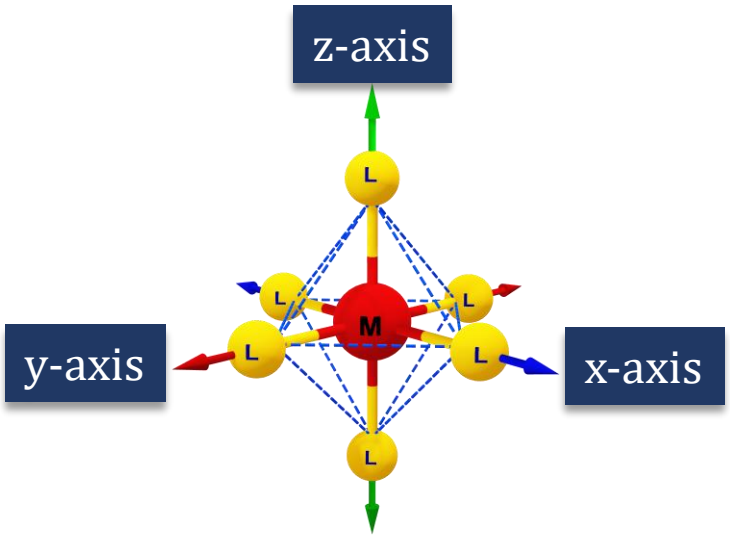
(c) The extent of splitting of metal d-orbitals depends upon the nature and number of ligands surrounding it and the charge on the central metal ion.

(d) The extent of splitting of metal d-orbitals determines the magnetic and spectroscopic properties of the complexes.

Splitting in octahedral complex

In a octahedral complex, the co-ordination number is 6. The metal ion is at the centre and the ligands occupy the six corners of the octahedron as shown in figure.

We know that two orbitals, and are oriented along the axis while the remaining three orbitals, viz., d_{xy}, d_{yz} and d_{zx} are oriented in between the axis.



The two orbtials and are designated as e_g orbitals while the three orbitals d_{xy}, d_{yz} and d_{zx} are designated as t_{2g} orbitals. As the six ligands approach the central ion along the axis hence e_g orbitals, is repelled more by the ligand than the t_{2g} orbitals.

In other words, the energy of the e_g orbitals increases much more than the energy of the t_{2g} orbitals.

Thus, in octahedral complexes, the five d-orbitals split up into two sets : one set consisting of two orbitals (and) of higher energy (e_g orbitals) and the other set consisting of three orbitals (d_{xy}, d_{yz} and d_{zx}) of lower energy (t_{2g} orbitals).

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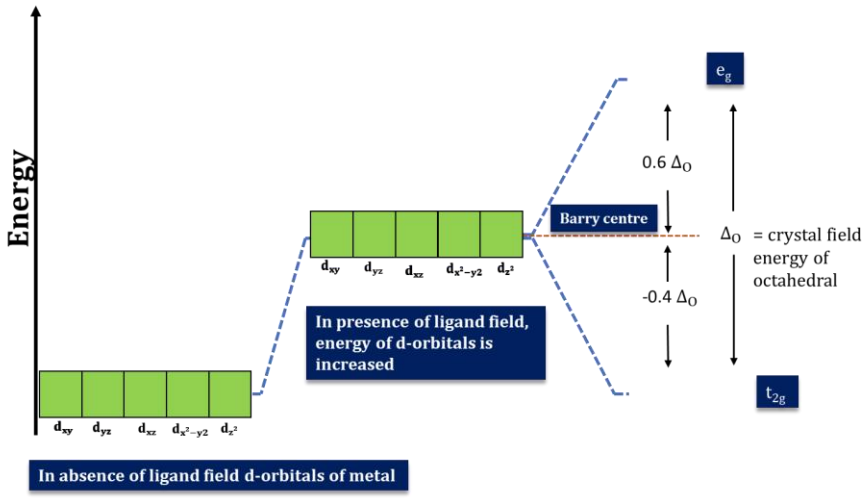


Calculation of crystal field stablizing energy

For octahedral complex CFSE = $\left[-0.4\left(n_{t_{2g}}\right)+0.6(n_{eg})\right]\Delta_0$ + x **pairing energy (P.E.)**

Where n_{2g} = number of electron in t_{2g} orbitals

n_{eg} = number of electron in e_g orbitals

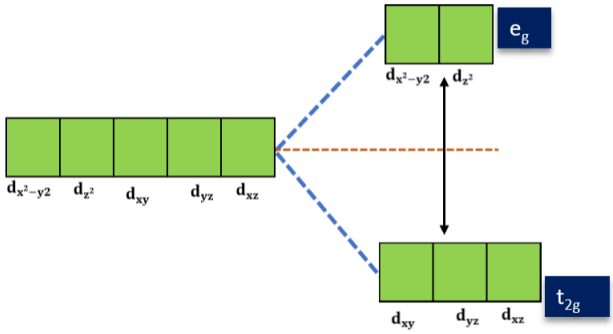
Δ_0 = crystal field **splitting** energy

x = number of electrons pairs in t_{2g} and e_g orbitals

Example: **Explain the formation of $Na_4[Fe(CN)_6]$ and $Na_4[FeF_6]$? Show which is low spin and which is high spin complex and also calculate the Crystal field stablisation energy (CFSE) ?**

Solution: In given compounds CN^- is strong field ligands and F^- is weak field ligand and in both compounds ions is in +2 oxidation state d^6 configuration.

So in **$Na_4[Fe(CN)_6]$**



$\because$ In presence of CN^- (SFL) Δ_0 is high than pairing energy, so unpaired e^- get paired and it is a low spin complex

CFSE = $[-0.4(6) + 0.6(0)]\Delta_0 + 3P$

= $-2.4\Delta_0 + 3P$

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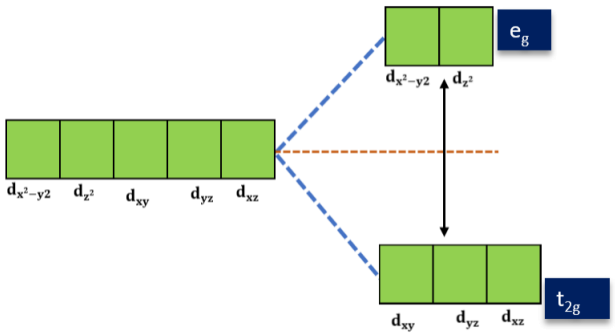
$Na_4[FeF_6]$



In presence of F^- (WFL) Δ_0 is less than pairing energy so unpaired e^- do not get paired and it is a high spin complex

CFSE = $[-0.4(5) + 0.6(2)]\Delta_0 + P$

= $[-2.0 + 1.2]\ \Delta_0 + P$

= $-0.8\ \Delta_0 + P$

Factors Affecting Splitting Energy

Factors affecting splitting energy (Δ)

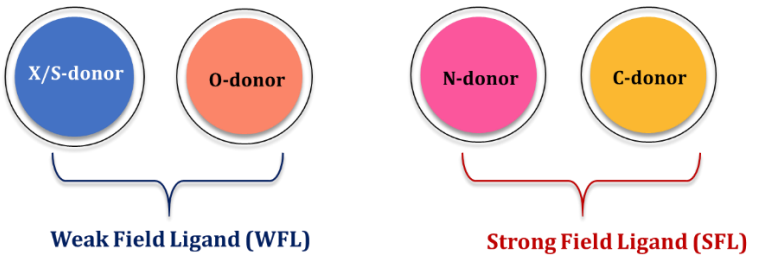
(1)	Strength of ligand	[C.F.S.E. is more in case of S.F.L. as compared to W.F.L.]
(2)	Oxidation state of central metal ion	[C.F.S.E. ∝ oxidation state]
(3)	Transition series (d-series)	[C.F.S.E., 5d > 4d > 3d]
(4)	Geometry (number of ligand)	[$\Delta_{sp} > \Delta_0 > \Delta_t$]

$\Delta_t = 4/9\ \Delta_0$ $\Delta_{sp} = 1.3\Delta_0$

Spectro-chemical series for ligands

Series which shows the relative strength of ligands

$I^- < Br^- < SCN^- < Cl^- < S^{-2} < F^- < OH^- < C_2O_4^{-2} < H_2O < NCS^- < EDTA^{-4} < NH_3 < en < NO_2^- < CN^- < CO$



Stability of co-ordination compounds

According to thermodynamic stability, the reaction between a metal ion and the ligands may be considered as a Lewis acid base reaction. If the equilibrium constant is high then the complex obtained is thermodynamically stable. The reaction can be written as follows : $M + nL \rightleftharpoons [ML_n]$

The stability constant K, of the complex $[ML_n]$ is given by the relation, $K = \frac{[ML_n]}{[M][L]^n}$

The greater the value of K, more stable is the complex.

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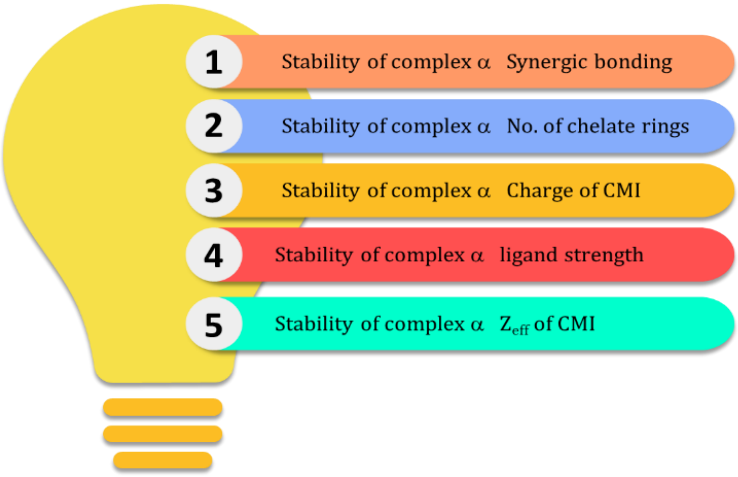
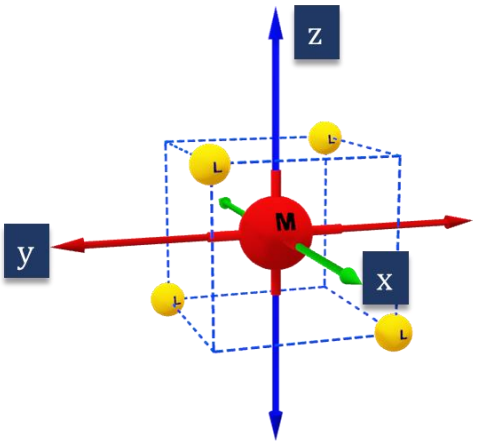
The stability of a complex ion also depends upon


1 Stability of complex α Synergic bonding
2 Stability of complex α No. of chelate rings
3 Stability of complex α Charge of CMI
4 Stability of complex α ligand strength
5 Stability of complex α Z_{eff} of CMI

CFT in Tetrahedral Complexes & Colour Properties

CFT in tetrahedral complexes

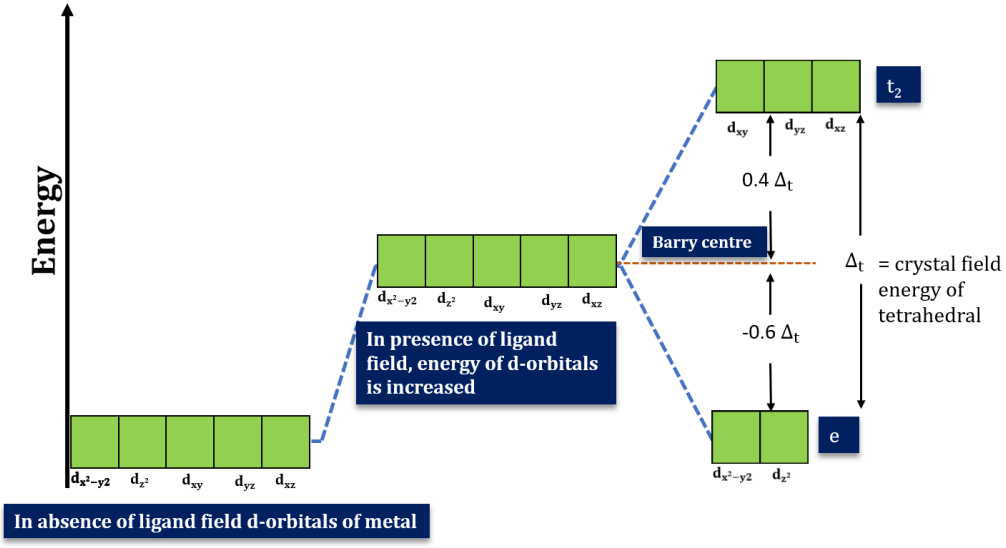
The co-ordination number for tetrahedral complexes is 4. The tetrahedral arrangement of four ligands surrounding a metal ion may be visualized by placing ligands at the alternate corners of a cube, as shown in figure.



It can be shown that in a tetrahedral structure, none of the d-orbitals points exactly towards the ligands.

When ligand approaches it is more close d_{xy}, d_{yz}, d_{xz} in comparision of d_{x2-y2} and d_{z2} because d_{xy}, d_{yz}, d_{zx} are between the axis and d_{z^2} and $d_{x^2-y^2}$ are along the axis. So d_{xy}, d_{yz}, d_{zx} feels more repulsion as compare to d_{z^2} and $d_{x^2-y^2}$.

Thus, the d orbitals are also splitted into two groups but in a reverse order of octahedral complex. The three orbitals, d_{xy}, d_{yz} and d_{xz}, designated are now have higher energy than the two orbitals.



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For tetrahedral complexes CFSE= $\left[-0.6\left(n_e\right)+0.4\left(n_{t_2}\right)\right]\Delta_t$ + x pairing energy (P.E)

where n_{t_2} = number of electron in t_2 orbitals

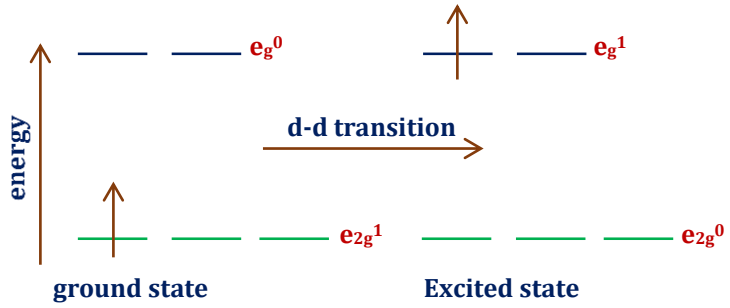
n_e = number of electron in e orbitals

Δ_t = crystal field **splitting** energy (tetrahedral)

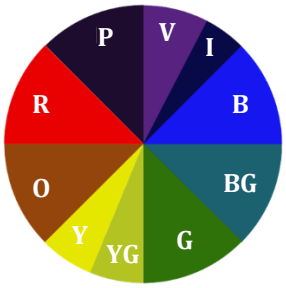
x = number of electron pairs in t_2 and e orbitals

Colour Property of Complex Compounds

Reason for colour in complexes is due to d-d-transition



Complementary colour wheel



For example complementary colour of **red** is **blue green**.

Example: **$[Ti(H_2O)_6]^{+3}$ is violet in colour explain using CFT.**

Solution: In $[Ti(H_2O)_6]^{3+}$, d-orbitals of Ti^{3+} lost their degeneracy in the presence of octahedral ligand field and produce t_{2g}^1 & eg^0 orbital of different energy, complex absorbs visible light for excitation of electron from t_{2g} to eg which is corresponding to green yellow colour and show its complimentry violet colour.

Example: **How the complex compounds show the colour?**

Solution: When d-electrons absorbs energy from visible region they will get excited. Absorbed energy is related to a particular wavelength.

$$E_{\substack{\text{absorbed}\\(\Delta)}} = \frac{hc}{\lambda_{absorbed}}$$

when electrons fall into lower energy level it will show colour whose wavelength (λ) is the complimentary of absorbed wavelength ($\lambda_{absorbed}$).

Example: **Why violet coloured $[Ti(H_2O)_6]Cl_3$ becomes colourless when heated ?**

Solution: When $[Ti(H_2O)_6]Cl_3$ is heated water molecules are removed and in the absence of ligand crystal field splitting does not occur and hence the substance is colourless due to absence of d–d transition.

Example: **$[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ show different colours. Why ?**

Solution: Due to difference in strength of ligands splitting energy will be different due to which $\lambda_{absorbed}$ and $\lambda_{emitted}$ will be different for both complexes.

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Example: **What will be the correct order for the wavelengths of absorption in the visible region for the following : $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?**

Solution: $[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$

Golden Key Points

- Red colour of ruby is due to presence of small amount of Cr^{+3} in atmosphere of Al_2O_3
- Green colour of emerald is due to presence of Cr^{+3} in atmosphere of $Be_3Al_2Si_6O_{18}$ [beryl]
- Complex become colourless in absence of ligand field because in absence of ligand d-d-transition does not occur.
- $[Ti(H_2O)_6]^{3+}$ become colourless on heating due to removal of water molecules.
- Anhydrous $CuSO_4$ which is colourless but hydrated $CuSO_4$ is blue in presence of moisture.
- Halogens are coloured due to the HOMO-LUMO transition.
- $KMnO_4$, $K_2Cr_2O_7$, CrO_2Cl_2 are coloured due to charge transfer spectrum.

BEGINNER'S BOX-4

1. Consider the following statements and choose correct code (T – True, F – False)

S_1 : $[Cr(NH_3)_6]^{3+}$ is a inner orbital complex with crystal field stabilization energy equal to $-1.2\ \Delta_o$

S_2 : The complex formed by joining the CN^- ligands to Fe^{3+} ion has theoretical value of 'spin only' magnetic moment equal to 1.73 B.M.

S_3 : Spin magnetic moment of complex $[Mn(CN)_6]^{-3}$ is 2.8 BM.

(1) F T F (2) T T F (3) T T T (4) F F F

2. For the $t_{2g}^6 e_g^2$ system, the value of magnetic moment (μ) is :

(1) 2.83 B.M. (2) 1.73 B.M. (3) 3.87 B.M. (4) 4.92 B.M.

3. Which of the following compound is not coloured :-

(1) $Na_2[CuCl_4]$ (2) $Fe_4[Fe(CN)_6]_3$ (3) $Na_2[CdCl_4]$ (4) Na_2CrO_4

4. The stability constants of the complexes formed by a metal ion M^{2+} with NH_3, CN^-, H_2O are of the order of 10^{15}, 10^{27}, 10^{11} respectively. Then :-

(1) NH_3 is the strongest ligand

(2) CN^- is the strongest ligand

(3) These values cannot predict the strength of the ligand

(4) All the ligands are equally strong

5. The value for crystal field stabilisation energy is zero for

(1) $K_2(MnF_6]$ (2) $K_3[Fe(CN)_6]$ (3) $K_3[FeF_6]$ (4) $K_4[Fe(CN)_6]$

6. Match the following and choose correct option

Complexes	**e⁻ configuration**
(P) $[CoCl_6]^{3-}$	(a) $t_{2g}^5 e_g^0$
(Q) $[Co(OX)_3]^{3-}$	(b) $t_{2g}^6 e_g^0$
(R) $[Co(H_2O)_6]^{2+}$	(c) $t_{2g}^5 e_g^2$
(S) $[Fe(CN)_6]^{-3}$	(d) $t_{2g}^4 e_g^2$

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	P	Q	R	S
(1)	b	a	c	d
(2)	d	a	b	c
(3)	d	b	c	a
(4)	d	a	c	b

7. Which order is correct

(1) $[NiCl_6]^{4-} > [NiCl_4]^{2-}$ splitting energy

(2) $[Cr(en)_3]Cl_3 > [Cr(H_2O)_6]Cl_3$ crystal field stabilisation energy

(3) $[Co(CN)_6]^{4-} > [Co(CN)_6]^{3-}$ reducing behaviour

(4) All of these

8. Which is inner orbital complex ?

(1) $[Co(H_2O)_6]^{3+}$ (2) $[RhF_6]^{3-}$ (3) $[IrF_6]^{3-}$ (4) All

9. Which stability order is incorrect

(1) $[Fe(C_2O_4)_3]^{3-} > [Fe(H_2O)_6]^{3+}$ (2) $[Fe(EDTA)]^{2-} > [Fe(en)_3]^{3+}$

(3) $[Ni(en)_2]^{2+} > [Ni(dmg)_2]$ (4) $[Fe(CN)_6]^{3-} > [Fe(CN)_6]^{4-}$

10. The complex exhibit lowest energy absorption band is

(1) $[NiCl_4]^{2-}$ (2) $[Ni(CO)_4]$ (3) $[Ni(CN)_4]^{2-}$ (4) $[Ni(H_2O)_6]^{2+}$

Isomerism

Isomerism in complexes

Compounds which have the same molecular formula, but differ in their properties due to the difference in their structure are called as **Isomers**.

Classification of isomerism :

(A) Structural Isomerism

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

(a) Ionisation Isomerism

Compounds having same molecular formula but give different type of ions in their aqueous solution are known as ionisation isomer.

Due to exchange of ions between coordination sphere and ionisation sphere different ionisation isomers are formed. So they are ionisation isomers.

Ex. (a) $CoBrSO_4 \cdot 5NH_3$ can be represented as

(i) $[Co(NH_3)_5Br]\ SO_4$ (red violet) **(ii)** $[Co(NH_3)_5\ SO_4]\ Br$ (red).

These complexes give sulphate ion and bromide ion respectively

(b) $[Pt(NH_3)_4Cl_2]\ Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

(c) $[Co(NH_3)_4(NO_3)_2]SO_4$ and $[Co(NH_3)_4SO_4](NO_3)_2$

(b) Hydrate Isomerism

This type of isomerism is due to presence of different number of water molecules inside the complex ion.

Ex. (1) $Cr(H_2O)_6Cl_3$ has three possible hydrate isomers.

(i) $[Cr(H_2O)_6]Cl_3$ (violet) **(ii)** $[Cr(H_2O)_5Cl]\ Cl_2 . H_2O$ (green)

(iii) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (dark green)

These complexes differ from one another with respect to the number of water molecules acting as ligands.

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(c) Linkage Isomerism

(i) This type of isomerism arises due to presence of ambidentate ligands

(ii) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

Ex. $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5\ ONO]Cl_2$

In NO_2^- ligand, the donor site is nitrogen while in ONO^- ligand donor site is oxygen.

(d) Coordination Isomerism

(i) This type of isomerism is exhibited when in complex compound both cation as well as anion is complex.

(ii) This type of isomerism is caused by the interchange of ligands between the two complex ions of a complex compound.

Ex. (i) $[Co(NH_3)_6]\ [Cr(CN)_6]$

(ii) $[Co(NH_3)_5\ (CN)]\ [Cr(CN)_5\ (NH_3)]$

} Coordination isomers

Trick to find number of coordination isomers

To find total coordination Isomers we can use the following method : -

(i) Different Central metal atom, same C.N., Monodentate ligand = C.N.

(ii) Same Central metal atom, same CN, Monodentate ligand = $\frac{C.N.}{2}$

(B) Stereo Isomerism

(a) They have same molecular formula, same constitution but they differ only with respect to the spatial orientation of ligands in space around the metal ion.

(b) The two types of stereo isomers which are possible are - Geometrical and optical.

(I) Geometrical Isomerism

(i) Due to change in relative positions of ligands around central metal ion, different forms are obtained which are known as GI.

(ii) When two identical ligands are coordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).

(iii) If the two identical ligands are coordinated to the metal ion from opposite side then it is **Trans isomer.**

(in Latin, Trans means across).

(iv) These geometrical isomers differ in physical as well as in chemical properties.

(v) Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.

(vi) 4-coordinated complexes with tetrahedral geometry do not exhibit cis - Trans isomerism, because relative position of ligands remain same for each other.

(vii) It is exhibited by 4-coordinated complexes with square planar geometry.

Note: There are only 5 possible cases which shows geometrical isomerism in square planar complex. such as Ma_2b_2, Ma_2bc, Mabcd, $M(AB)_2$, M(AB)cd

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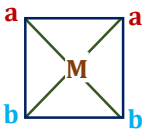
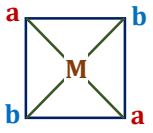
Geometrical Isomers with Coordination Number = 4 (Square Planar Complexes)

(i) Complexes with general formula, Ma_2b_2 (where both a and b are monodentate) can have Cis-and trans isomers.

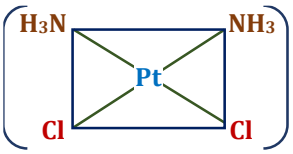


Cis-isomer

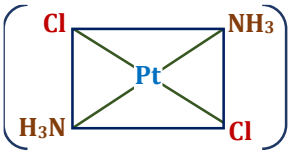


Trans-isomer

Ex. $[Pt(NH_3)_2Cl_2]$

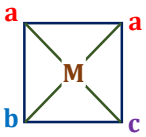


cis-platin
(used as a anti-cancer)

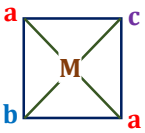


Trans-platin

(ii) Complexes with general formula Ma_2bc can have Cis - and trans-isomers.

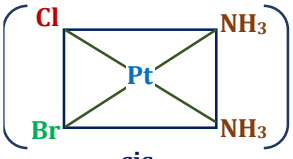


Cis

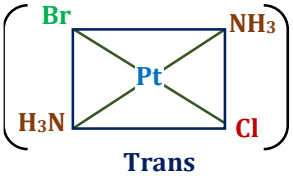


Trans

Ex. $[Pt(NH_3)_2ClBr]$



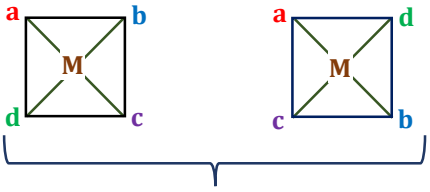
cis



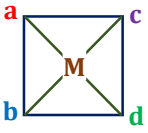
Trans

(iii) Complexes with general formula, **Mabcd** can have three geometrical isomers.

e.g. $[Pt(NH_3)(Py)ClBr]$



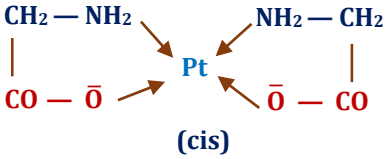
cis (w.r.t ligand a & d)



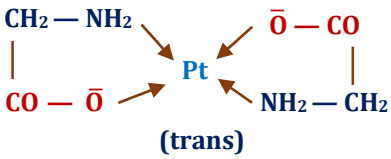
Trans (w.r.t. ligand a & d)

(iv) Complex with general formula $[M(AB)_2]$ have 2 geometrical isomers (Where AB is unsymmetrical Bidentate ligand)

e.g. $[Pt(gly)_2]$



(cis)



(trans)

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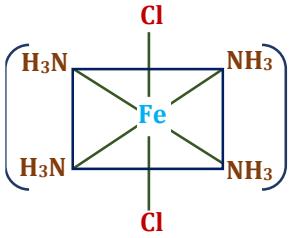
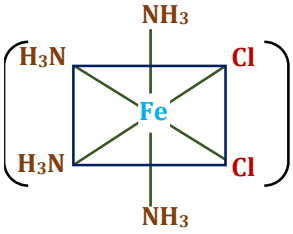
Geometrical isomers with Coordination number = 6 (Octahedral complex)

(i) $[Ma_4b_2]$ has 2 geometrical isomers

e.g. $[Fe(NH_3)_4Cl_2]$



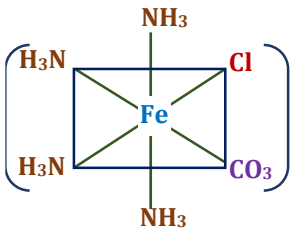
Trans



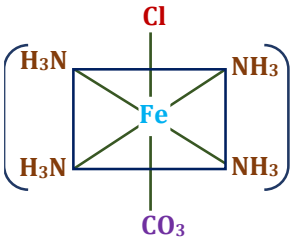
Cis

(ii) $[Ma_4bc]$ has 2 geometrical isomers

e.g. $[Fe(NH_3)_4ClCO_3]$



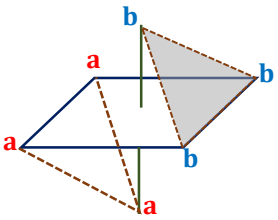
Cis



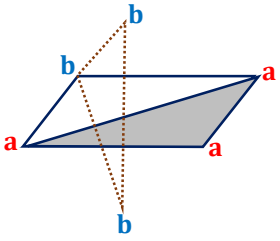
Trans

(iii) Facial and Meridional isomerism (Ma_3b_3)

eg. $[Cr(NH_3)_3(H_2O)_3]^{+3}$



Facial (fac)



Meridional [Mer]

Other examples of geometrical isomers in octahedral complexes.

General formula	Total No. of geometrical isomers
Ma_6	Nil
Ma_5b	Nil
Ma_4b_2	2
Ma_4bc	2
Ma_3b_3	2
Ma_3b_2c	3
Ma_3bcd	4
$Ma_2b_2c_2$	5
Ma_2b_2cd	6
Ma_2bcde	9
$Mabcdef$	15

Here M = central metal atom; a, b, c, d, e, f = Monodentate ligands

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(II) Optical Isomerism

(i) Compounds which are mirror image of each other but non-superimposable, are known as optical isomers.

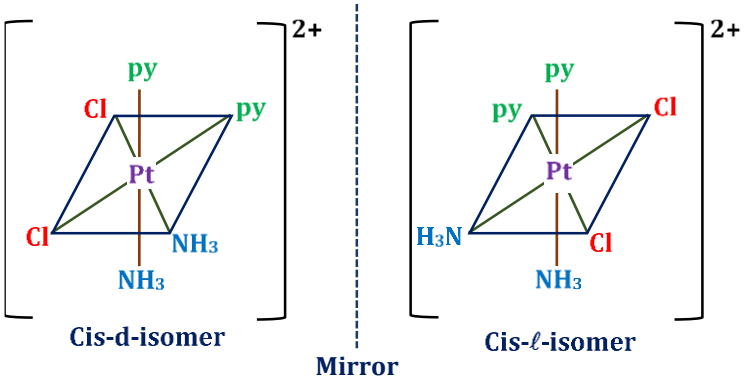
(ii) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.

(iii) The complex which rotates plane polarised light to left hand side is **laevo rotatory i.e. 'ℓ' or '–'** and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory 'd' or '+'**. (d) Thus, complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.

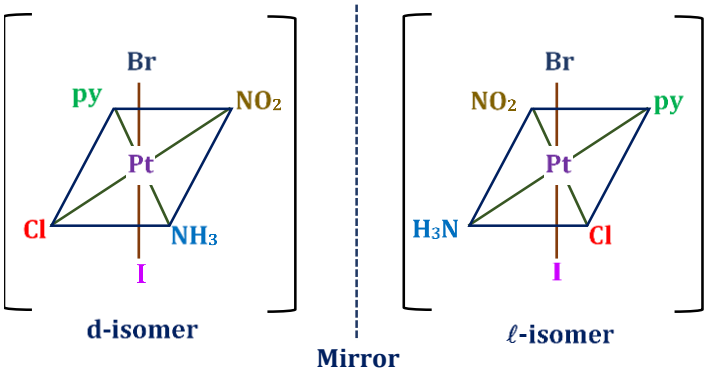
(iv) The 'd' and 'ℓ' isomers of a compound are called as **Enantiomers**.

Optical isomers with Coordination number = 6

(i) $[Ma_2b_2c_2]^{n+} \rightarrow [Pt(py)_2(NH_3)_2Cl_2]^2$



(ii) $[Mabcedf] \rightarrow [Pt(py)NH_3NO_2ClBrI]$



Total number of geometrical isomers = 15 (All are optically active)

Total number of optical isomers = 30

Total number of stereo isomers = 30

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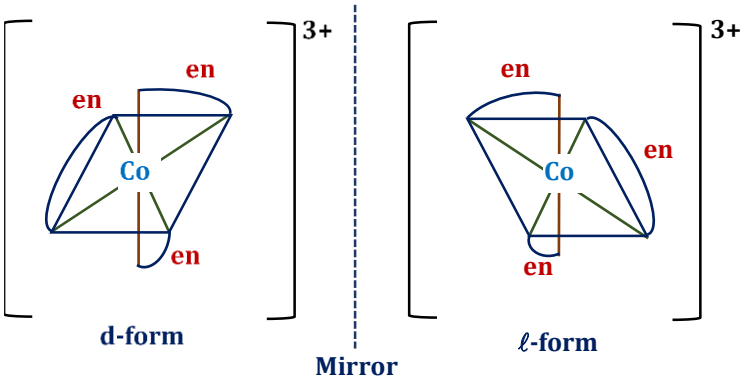
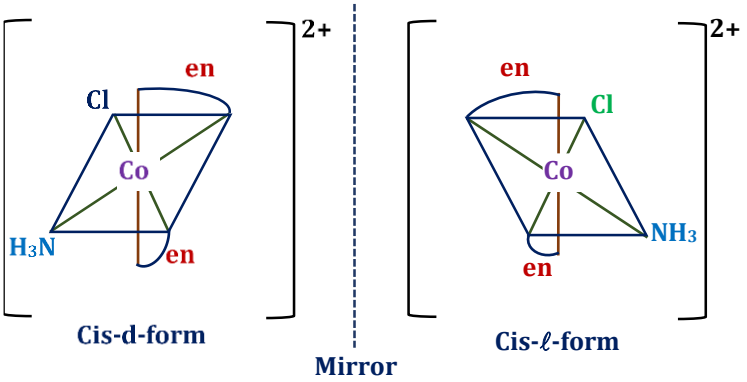
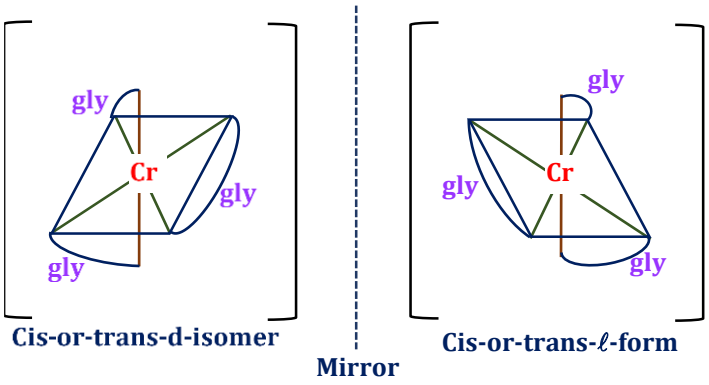
(iii) $[M(AA)_3]^{n+} \rightarrow [Co(en)_3]^{3+}$



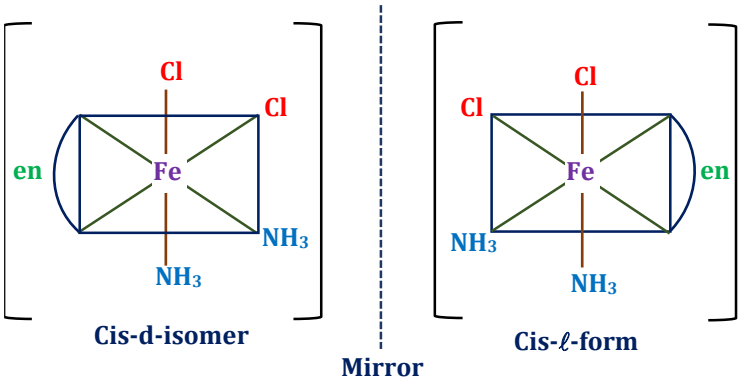
(iv) $[M(AA)_2ab]^{n+} \rightarrow [Co(en)_2NH_3Cl]^{2+}$



(v) $[M(AB)_3] \rightarrow [Cr(gly)_3]$



(vi) $[Fe(NH_3)_2(en)Cl_2]$



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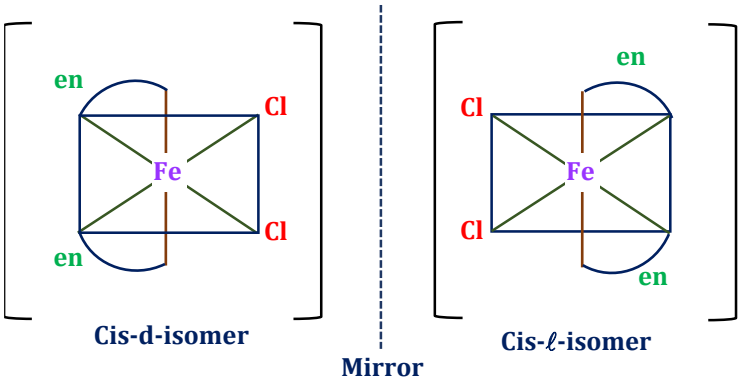
(vii) $[Fe(en)_2Cl_2]$



BEGINNER'S BOX-5

1. Which of the following sets is/are example of co-ordination isomerism in complexes ?

(1) $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Co(CN)_6]$ $[Cr(NH_3)_6]$

(2) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

(3) $[Co(NH_3)_5Br]SO_4$ and $[Cr(NH_3)_5SO_4]Br$

(4) $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4]$ $[PtCl_4]$

2. The number of geometrical isomers of $[Co(NH_3)_3(NO_3)_3]$ are :

(1) 0 (2) 2 (3) 3 (4) 4

3. The number of isomeric forms in $[Co(NH_3)_4Cl_2]^{1+}$ ion will be :-

(1) 2 (2) 3 (3) 4 (4) 1

4. The total number of possible coordination isomers for the complex compound $[Cu(NH_3)_4]$ $[PtCl_4]$

(1) 3 (2) 6 (3) 5 (4) 4

5. The complexes $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(ONO)(NH_3)_5]Cl_2$ are the examples of

(1) Coordination isomerism (2) Ionisation isomerism

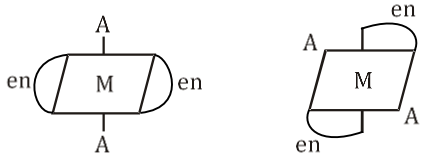
(3) Geometrical isomerism (4) Linkage isomerism

6. The type of isomerism exhibited in complex $[Pt(NH_3)_4Cl_2]Br_2$ is/are

(1) Linkage isomerism (2) Ionisation isomerism

(3) Geometrical isomerism (4) 2 and 3 both

7. The Complexes given below are :



(1) Geometrical isomers (2) Position isomers

(3) Optical isomers (4) Identical

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Organo Mettalic Compound

Compound in which C atom of a hydrocarbon or a ligand is directly bonded with a metal/ metalloid / non-metal like B, P ets is known as organometallic compounds.

eg. **R - Zn - R dialkyl zinc (Frankland reagent)**
R - Mg - X Alkyl Magnesium halide (Grignards reagent) } **OMC**

Sodium acetate	$CH_3-\overset{\overset{O}{\|\|}}{C}-ONa$
Sodium ethoxide	C_2H_5-O-Na
Sodium Mercaptide	H_3C-SNa

These are not organometallic compounds because in these compounds metal is not directly attached with carbon atom.

$B(OCH_3)_3$ (H_3CO, H_3CO, $B-OCH_3$) **is not OMC** $CH_3B(OCH_3)_2$ (H_3C-B, OCH_3, OCH_3) **is OMC**

Carbides and carbonates are not considered OMC because in these compounds metal carbon bond has ionic nature.

Classification of Organometallic Compounds

OMC can be classified into three main categories –

σ - bonded OMC : These compounds are formed mostly by non-transition and metalloid elements.

Ex. **$R-Mg-X$** (Grignard's reagent)
$(CH_3)_2Zn$ (Dimethyl zinc or Frankland's reagent)
R_2Cd (dialkyl cadmium)
$(C_2H_5)_4Pb$ (Tetra ethyl lead) – used as antiknocking agent in petrol.
$(C_2H_5)_3Al + TiCl_4$ (Ziegler natta catalyst) – Heterogeneous catalyst, used in polymerisation of alkene.

π - bonded OMC : These are usually formed by transition metals.

Ex. Ferrocene **$[Fe(\eta^5-C_5H_5)_2]$**
Zeise's salt **$K[PtCl_3(\eta^2-C_2H_4)]$**
Chromocene **$[Cr(\eta^6-C_6H_6)_2]$**

σ and π - bonded OMC : Transition metals of gp. 6, 7, 8, 9 and 10 in their zero-oxidation state form such type of OMC. The carbonyl compounds of these metals have both σ and π bonds.

Ex. **$[Ni(CO)_4]$**, **$[Fe(CO)_5]$**, **$[Mn_2(CO)_{10}]$** etc.

Application Of Complexes

(a) **Test of Ni^{+2}** : Ni^{+2} ion gives rosy red ppt when react with dimethylglyoxime in weak alkaline medium.

$$Ni^{+2} + 2dmg \xrightarrow{NH_4OH} \underset{\text{Rosy Red ppt}}{[Ni(dmg)_2]}$$

(b) **Test of S^{2-}** :

$$\underset{\text{Sodium nitro prousside}}{Na_2[Fe(CN)_5(NO)]} + Na_2S \rightarrow \underset{\text{violet colour}}{Na_4[Fe(CN)_5(NOS)]}$$

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(c) **Test of Fe^{+2} & Fe^{+3} :**

$$\underset{\text{salt}}{Fe^{+2}} + \underset{\text{1,2-drops}}{K_3[Fe(CN)_6]} \rightarrow \underset{\text{turn bull blue}}{Fe_3[Fe(CN)_6]_2} \xrightarrow{K_3[Fe(CN)_6]} \underset{\text{colloidal soluton}}{3KFe[Fe(CN)_6]}$$

$$\underset{\text{salt}}{Fe^{+3}} + \underset{\text{1,2-drops}}{K_4[Fe(CN)_6]} \rightarrow \underset{\text{prussium blue}}{Fe_4[Fe(CN)_6]_3} \xrightarrow{K_4[Fe(CN)_6]} \underset{\text{colloidal soluton}}{4KFe[Fe(CN)_6]}$$

(d) **Test of Fe^{+3}**

$$FeCl_3 + \underset{\text{Potassium thiocyanate}}{3KSCN} \rightarrow \underset{\text{Blood red colour}}{Fe(SCN)_3} + 3KCl$$

(e) **Test of Cu^{+2}**

$$2Cu^{+2} + K_4[Fe(CN)_6] \rightarrow \underset{\text{Chocolate brown ppt}}{Cu_2[Fe(CN)_6]}$$

(f) **Brown ring test : Test for Nitrate ion**

$NO_3^- + Fe^{+2} + 4H^+ \longrightarrow Fe^{+3} + NO + 2H_2O$ (Redox reaction)

$$[Fe(H_2O)_6]SO_4 + NO \rightarrow \underset{\text{brown ring complex}}{\left[Fe(H_2O)_5(\overset{+}{N}O)\right]SO_4}$$

(g) If excess of KCN is added in $CuSO_4$, insoluble CuCN is formed which later turn into soluble complex.

$$\underset{\text{salt}}{2KCN} + \underset{\text{salt}}{CuSO_4} \xrightarrow[-K_2SO_4]{} \overset{+2}{Cu}(\overset{-1}{C}N)_2 \xrightarrow{\text{redox}} CuCN\downarrow + \frac{1}{2}(CN)_2 \text{(Cyanogen)}$$

$$\downarrow KCN(\text{excess})$$

$$\underset{\text{soluble complex}}{K_3[Cu(CN)_4]}$$

(h) AgCl or AgBr ppt are soluble in ammonia or NH_4OH

$$\underset{\text{white ppt}}{AgCl} \xrightarrow{2NH_3} \underset{\text{soluble complex}}{[Ag(NH_3)_2]^+} Cl^-$$

(i) In photography : undecomposed AgBr (at the time of image development) is removed from photographic film by using hyposolution [$Na_2S_2O_3.5H_2O$]

$$AgBr \xrightarrow{h\nu} Ag + \frac{1}{2}Br_2$$

$$\underset{\text{(undecomposed)}}{AgBr} + 2Na_2S_2O_3 \longrightarrow Na_3\underset{\text{soluble complex}}{\left[Ag(S_2O_3)_2\right]^{3-}} + NaBr$$

(j) Light blue colour of aqueous solution of $CuSO_4$ turn into dark blue in presence of ammonia

$$\underset{\text{light blue}}{[Cu(H_2O)_4]}SO_4 \xrightarrow{4NH_3} \underset{\text{dark blue}}{[Cu(NH_3)_4]}SO_4$$

(k) Cyano complex are used for electroplating of Ag or Au due to high stability.

e.g. $[Ag(CN)_2]^-$

(l) **Wilkinson catalyst** $[RhCl(PPh_3)_3]$ is used for hydrogenation of alkene. (Homogeneous catalysis)

(m) $[EDTA]^{4-}$ is used for **estimation of hardness of water**.

(n) $[Ca(EDTA)]^{2-}$ is **used to remove Pb poisoning**.

$$[Ca(EDTA)]^{2-} + Pb^{+2} \rightarrow [Pb(EDTA)]^{2-} + Ca^{+2}$$

(o) **Biological importance**

Chlorophyll (Mg)	haemoglobin (Fe^{+2})	Insulin (Zn)
Vitamin B_{12}(Co)	Corboxypeptide (Zn)	

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BEGINNER'S BOX-6

1. $K_4[Fe(CN)_6]$ reacts with $FeCl_3$ to form :-
(1) $K_3[Fe(CN)_6]$ (2) $K_4[Fe(CN)_3Cl_3]$ (3) $K_3[Fe(CN)_5Cl]$ (4) $KFe[Fe(CN)_6]$

2. A reagent used for identifying nickel ion is :-
(1) Potassium ferrocyanide (2) Phenolphthalein
(3) Dimethyl glyoxime (4) EDTA

3. A person suffering from lead poisoning should be fed with :-
(1) Hypo (2) Cis-platin (3) $[Ca(EDTA)]^{2-}$ (4) DMG

4. Zeigler natta catalyst is :
(1) $[RhCl(PPh_3)_3]$ (2) $Al(C_2H_5)_3 + TiCl_4$ (3) $K(PtCl_3(\eta^2 - C_2H_4)]$ (4) Pt/Rh

5. Which is/are organometallic compound :-
(I) Grignard reagent (II) Sodium methoxide (III) trimethyl boron (IV) TEL
(1) Only I (2) I & II (3) I, II, IV (4) I, III, IV

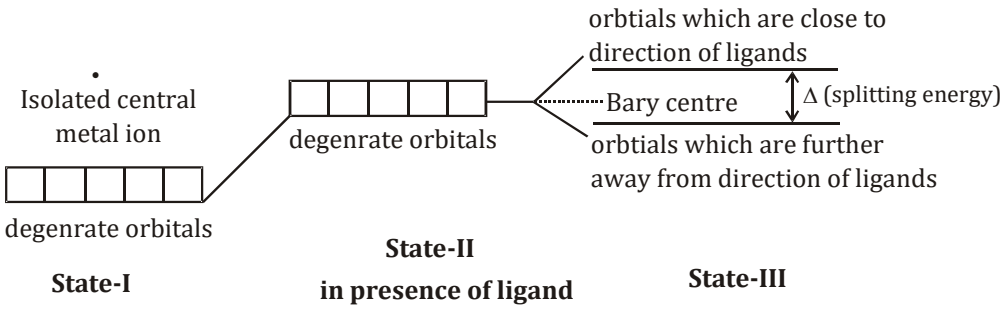
NCERT QUESTIONS

Q.1 Explain the term Degenerate orbitals :

Ans. Orbitals which have same energy in a subshell are known as degenerate orbitals.

Q.2 What is crystal field splitting ?

Ans. According to CFT the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and negative charge of ligand.
As a ligand approaches the metal ion, the electrons of ligand will repell some of the d-orbitals as compared to other d orbitals due to which energy of all d orbitals is not equal and they are splitted into different energy levels.
This loss of degeneracy of d-orbital is known as crystal field splitting.



The state I represents degeneracy of all the five d-orbitals in the isolated central ion. The state II represents hypothetical degeneracy of all the orbitals at a higher energy level if the negative charge of all the ligands is assumed to be uniformly affecting the electrons in the d-orbitals of the metal ion. The state III represents crystal field splitting of d orbitals.

Q.3 Define (a) crystal field stabilisation energy (b) Pairing energy ?

Ans. **(a) Crystal field stabilisation energy :** The lowering in the energy of a transition metal ion in presence of ligand environment due to crystal field effects.

(b) Pairing energy : The energy required to pair up the electrons.

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Q.4 Explain the term

(a) Inner orbital complex and outer orbital complexes ?

(b) Low spin and high spin complexes ?

Ans. (a) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and these complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively.

For example in d^2sp^3 hybridisation (n–1)d, ns and np orbitals are mixed it forms inner orbital complex and in sp^3d^2 ns, np and nd orbitals are mixed so it forms outer orbitals complex.

(b) When the strong field ligand approaches to metal ion, value to splitting energy (Δ) is greater than pairing energy, so it is unfavourable to put electron into high energy orbitals. Therefore, the lower energy orbitals are completely filled before distribution of the upper sets starts according to the Aufbau principle. Such type of complexes are called low spin complex.

Weak field ligand causes a small splitting of the d-orbitals where splitting energy is less than pairing energy. It is easier to put electrons into the higher energy set of orbitals than to pair up in the same low energy orbitals. So one electron is put into each of the five d-orbitals before any pairing occur in accordance with Hund rule.

Such complexes are known as high spin complex.

Q.5 In octahedral complex if central metal have configuration d^1, d^2, d^3 always make inner orbital complex, Why ?

Ans. Central metal ion which have d^1, d^2, d^3 configuration have at least two vacant d orbitals (e_g) in any ligand environment or in any oxidation state. So always form inner orbital complex.

Q.6 Calculate the spin magnetic moment (μ) into following complexes.

$[Cr(H_2O)_6]^{3+}$ $[Fe(H_2O)_6]^{3+}$ $[Zn(H_2O)_6]^{2+}$

Ans. In all compound H_2O is a weak field ligand so pairing of electron will not occur

(I) $[Cr(H_2O)_6]^{3+}$ (II) $[Fe(H_2O)_6]^{3+}$ (III) $[Zn(H_2O)_6]^{+2}$

e_g^0 ☐☐ e_g^2 1 1 e_g^4 ↿⇂ ↿⇂

t_{2g}^3 1 1 1 t_{2g}^3 1 1 1 t_{2g}^6 ↿⇂ ↿⇂ ↿⇂

n = 3 n = 5 n = 0

So by using formula $\sqrt{n(n+2)}$ we will get

$\mu = \sqrt{15}$ BM $\mu = \sqrt{35}$ BM $\mu = 0$

Q.7 Why the d^8 configuration always shows paramagnetism 2.83 B.M in octahedral complex?

Ans. In given d^8 configuration for octahedral complex for both strong field ligand and weak field ligand is always have two unpaired electron.

1 1 e_g 1 1 e_g

↿⇂ ↿⇂ ↿⇂ t_{2g} ↿⇂ ↿⇂ ↿⇂ t_{2g}

in case of Strong field ligand in case of Weak field ligand

n = 2 n = 2

$\mu = \sqrt{n(n+2)}$ B.M. $= \sqrt{2(2+2)} = 2.83$ B.M.

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BEGINNER'S BOX — ANSWERS KEY

BEGINNER'S BOX-1								
	Que.	1	2	3	4	5	6	7
	Ans.	**3**	**4**	**1**	**3**	**2**	**2**	**3**

BEGINNER'S BOX-2											
	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	**2**	**3**	**3**	**4**	**3**	**4**	**4**	**1**	**2**	**3**
	Que.	11	12								
	Ans.	**2**	**4**								

BEGINNER'S BOX-3											
	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	**4**	**2**	**2**	**3**	**1**	**4**	**1**	**2**	**4**	**3**

BEGINNER'S BOX-4											
	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	**3**	**1**	**3**	**2**	**3**	**3**	**4**	**4**	**3**	**1**

BEGINNER'S BOX-5								
	Que.	1	2	3	4	5	6	7
	Ans.	**1**	**2**	**1**	**4**	**4**	**4**	**4**

BEGINNER'S BOX-6						
	Que.	1	2	3	4	5
	Ans.	**4**	**3**	**3**	**3**	**2**

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